Inverse martensitic transformation in Zr nanowires

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Like martensitic transformations (MTs), inverse martensitic transformations (IMTs) are shear-dominant diffusionless transformations, but are driven by reduction in interfacial energies rather than bulk free energies, and exhibit distinctive behavior such as instantaneous initiation (like spinodal decomposition) and self-limiting lengthscale. Bulk Zr metal is known to undergo normal MT from the high-temperature bcc phase to the low-temperature hcp phase. Using molecular dynamics simulations we demonstrate that, unlike in the bulk, an IMT to the bcc structure can occur in ⟨1100⟩-oriented hcp Zr nanowires at low temperatures, which is driven by the reduction in the nanowire surface energy. The bcc domains subsequently become distorted and transform into a new ⟨1120⟩-oriented hcp domain, leading to reorientation of the nanowire. This behavior has implications for the study of structural transformations at the nanoscale and surface patterning.

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I. INTRODUCTION

Martensitic transformation (MT) is a well-known diffusionless transition that occurs in materials undergoing solid-to-solid phase changes.1–4 On the basis of Zener’s model,1 the parent phase is stable at high temperatures and usually has a relatively open structure which transforms into the (often more close packed) product phase upon cooling below a martensite-start temperature. Pure Zr, for example, undergoes such a MT from the high-temperature bcc structure to the low-temperature hcp phase, which is the most stable bulk phase at 0 K. This transition has been well studied in the bulk and follows the mechanism originally proposed by Burgers.5

In classic MT nucleation [Fig. 1(a)],6 the bulk energy \( V\Delta g_{\text{bulk}} < 0 \) is the driving force (proportional to the transformed volume \( V \)), whereas the interfacial energy \( \Delta \bar{\gamma} > 0 \) (proportional to the area \( A \) of the transformed region, where \( \bar{\gamma} = \frac{\Sigma_{\gamma} a_i}{\Sigma A_i} \) is averaged over all interfaces that may include surfaces, where \( V, A_i \) are the pre-transformed volume and areas, respectively, even for post-transformed configuration, i.e., Lagrangian measure of \( \Delta g_{\text{bulk}}, \bar{\gamma} \) works against the bulk driving force, from which one can derive a positive saddle energy. This means that for any finite driving force \( \Delta g_{\text{bulk}} < 0 \), there is a positive activation barrier energy and waiting time for the nucleation of martensite, according to the reaction rate theory for the formation of the critical nucleus.7 Once the activation barrier is overcome, the system transforms in a downhill process, with no bounds on the transformation \( V \).

In inverse martensitic transformations (IMTs), the interfacial energy becomes the driving force and the bulk energy now works against the transformation, as shown in Fig. 1(b). Here \( \Delta \bar{\gamma} < 0, \Delta V g_{\text{bulk}} > 0 \); both are inverted from those of normal MT, hence the name IMT. Two consequences can be seen from Fig. 1(b): (a) there is no nucleation barrier for IMT, i.e., IMT can happen instantaneously the moment \( \Delta \bar{\gamma} \) turns negative and (b) IMT will stop automatically at a certain length scale \( r^* \propto \Delta \bar{\gamma}/\Delta g_{\text{bulk}} \), as the rising bulk energy prevents further transformation. Thus, unlike isothermal MT which waits for a while (and therefore requires finite undercooling to be observable at laboratory time scale) but then keeps going once the barrier is overcome, IMT should happen nearly instantaneously but self stops at \( r^* \).

Similar energetics as Fig. 1(b) is found in surface premelting phenomena, and is the reason that the melting of simple metals typically requires no superheating, whereas their solidifications require finite undercooling, as indicated by the time-temperature-transformation diagrams.7 The difference is that surface premelting is a diffusive process whereas IMT is diffusionless. Therefore, IMT should be observable at low temperatures as diffusion is not required. In a semi-infinite half-space (height \( h = \infty \) with open surface, the elasticity aspect of IMT and the finite length scale \( r^* \) may be utilized to introduce nanoscale patterning of the surface. If the sample

FIG. 1. (Color online) A comparison of the free energy landscape for (a) the normal MT and (b) the IMT, where \( r^* \) is characteristic size of the transformed region. In (a), the driving force is the bulk free energy \( V\Delta g_{\text{bulk}} < 0 \) and the interfacial energy \( \Delta \bar{\gamma} > 0 \) opposes the transformation. In (b), the interfacial energy \( \Delta \bar{\gamma} < 0 \) provides the driving force whereas the bulk free energy \( V\Delta g_{\text{bulk}} > 0 \) opposes it.
length scale $H$ is comparable or smaller than $r^*$, however, IMT can be expected to finish throughout the sample (see our simulation below).

In this paper, we demonstrate such IMT at room temperature (RT), on the surface of Zr nanowires (NWs). In contrast to the normal MT where bcc transforms to hcp, a hcp to bcc transition is found instead, driven by the minimization of the surface energy of the NW, which becomes controlling for systems with very large surface-to-volume ratio. The surface energy minimization is accomplished via a two-step process: the initial $(\bar{1}100)$-oriented Zr nanowire first undergoes IMT to the bcc configuration and becomes distorted, and subsequently undergoes a normal MT to a new $(\bar{1}120)$-oriented hcp configuration. Similar surface-driven structural changes, such as crystal reorientation via twinning, have been revealed by molecular dynamics (MD) simulations in fcc (Au, Cu) (Refs. 8–10) and bcc (W) (Ref. 11) metallic NWs.

II. METHODS

We have used embedded atom method potentials for Zr (Refs. 12 and 13) to perform the MD simulations. These potentials reproduce very well the properties such as the cohesive energy, elastic constants, and especially the MT between bcc and hcp. In the following, we show the results obtained using the Zr potential developed by Mendelev and Ackland.13 We first created the hcp $(\bar{1}100)$-oriented nanowire with orientations of $x$-[1100], $y$-[1120], and $z$-[0001] at 0 K. The cross section of the nanowire ($y$ and $z$ axes) is close to square with the [0001] side length in the range of 1.0–2.6 nm. The initial length of nanowire ($x$ axis) is a factor of ten larger than the length of the cross section. The wire is then heated to 300 K at the rate of 100 K/ps and then relaxed at 300 K for 50 ps using the Nosé-Hoover thermostat.14,15 During the above process, free boundary condition in three dimensions is used. The MD calculation is carried out using the LAMMPS code16 with the atomic configurations displayed using ATOMEYE.17

III. RESULTS AND DISCUSSION

When the $(\bar{1}100)$-oriented Zr NW is relaxed at 300 K for several picoseconds, the initial hcp configuration spontaneously undergoes IMT to transform to the bcc structure ($x$-[101], $y$-[010], and $z$-[101]). As seen in Figs. 2(a) and 2(b), the bcc phase initiates on {1120} surface planes in the middle section of the wire and then spreads toward the ends and the interior. With the bcc formation, the phase boundaries divide the wire into three phase domains, one with the bcc structure at the center of the NW and the others with hcp structure at the ends. However, the phase boundaries do not move across the whole wire to convert the entire wire into the bcc phase, which undergoes severe compressive deformations along the wire axis to a new hcp configuration ($x$-[010], $y$-[101], and $z$-[101]), as shown in Fig. 2(c). Finally, the distorted bcc phase gives way to a new $<\bar{1}120>$-oriented hcp configuration ($x$-[1120], $y$-[1100], and $z$-[0001]) in a normal bcc-to-hcp MT [Fig. 2(d)]. Compared to the initial $(\bar{1}100)$ wire, the $(\bar{1}120)$-oriented hcp unit cell can be considered to have rotated 30°, and this crystal reorientation is not completed directly by twinning as in fcc (Refs. 8–10) and bcc nanowires11 but via the two-step IMT-MT processes shown above.

Aside from the energetic aspects, the transformation path itself is quite different because unlike the Bain path or the Burgers path in usual MT, the transformation path here is not a straight line in the six-dimensional strain space but contains a turn in strain space. The initial $(\bar{1}100)$-oriented and transformed $(\bar{1}120)$-oriented NWs are connected via an intermediate, distorted bcc phase, similar to the role of a stacking fault in the splitting of a full dislocation. Although the
bce domains initially merge into one, shown in Fig. 2(c), it subsequently splits into four triangle-shaped bce domains in Fig. 2(d). Two triangle-shaped bce domains on one side then form a soliton like “transformation front” that translates along the nanowire (speed ~200 m/s) and converts the $\langle 1\bar{1}00\rangle$ wire to the new $\langle 1\bar{1}20\rangle$ orientation. The unique geometry of this transformation front (two bce wedges) can be attributed to the quasi-one-dimensional nature of the nanowire and elasticity interaction associated with it, which cannot be seen in three-dimensional martensitic transformations. Conceptually, the two transformation fronts on left and right are analogous to a dislocation dipole of plus and minus full Burgers OR each with some core splitting, except the soliton translation accomplishes lattice rotation of the hcp phase rather than lattice slip [Fig. 2(d)]

The two-step IMT-MT processes shown above are driven by the reduction in surface energy. For the present $\langle 1\bar{1}00\rangle$-oriented hcp nanowire (21.1 nm × 2.1 nm × 2.1 nm), the surface energy of the initial $\langle 1\bar{1}00\rangle$-oriented wire is 0.379 eV/atom, which is higher than that of transformed bce (0.347 eV/atom) and that of $\langle 1\bar{1}20\rangle$-oriented bce configuration (0.295 eV/atom). The reduction of surface energy drives the phase change from the initial $\langle 1\bar{1}00\rangle$-oriented hcp wire to the bce and then the $\langle 1\bar{1}20\rangle$-oriented bce wire. Once the initial $\langle 1\bar{1}00\rangle$ wire is converted to the $\langle 1\bar{1}20\rangle$ wire, the system becomes stable and cannot revert back to the initial $\langle 1\bar{1}00\rangle$ orientation.

The hcp-bce IMT also follows the Burgers orientation relationship (OR), $\langle 0001\rangle_{\text{hcp}}\parallel\langle 0\bar{1}1\rangle_{\text{bce}}$ and $\langle 1\bar{1}20\rangle_{\text{hcp}}\parallel\langle 1\bar{1}1\rangle_{\text{bce}}$, as is the case for the normal bce-hcp MT that combines shear and shuffle operations. Specifically, two equivalent shear operations along the $[2\bar{1}10]$ and $[\bar{1}2\bar{1}0]$ change the 120° angle in the hcp phase to the 109.47° angle in the bce phase. Atoms also shuffle along the hcp $[1\bar{1}00]$ direction with displacement $\sqrt{3}a_0/6$ ($a_0$ is the lattice constant) to arrive at the bce structure.

Our present observation of IMT is analogous to the asymmetry between solidification and melting of simple metals, where the liquid-to-crystal transformation requires finite undercooling, $\Delta T = T_M - T > 0$, to overcome the nucleation barrier. However, the reverse crystal-to-liquid transition requires no superheating ($\Delta T = 0$) and can occur immediately when the bulk melting point ($T_M$) is reached, as long as a surface is present and

$$\gamma_S > \gamma_L + \gamma_{\text{LS}},$$  \hspace{1cm} (1)

where $\gamma_S$ is the solid surface energy, $\gamma_L$ is the liquid surface energy, and $\gamma_{\text{LS}}$ is the liquid-solid interfacial energy. Equation (1) basically means the solid surface can be completely wet by its own liquid. If Eq. (1) is satisfied, there will be a thin disordered layer on the crystal surface (surface premelt), even for $T < T_M$. For our hcp-to-bce case, a condition similar to Eq. (1) controls the IMT, i.e.,

$$\gamma_{\text{hcp}} > \gamma_{\text{bce}} + \alpha \gamma_{\text{hcp}}\sqrt{3},$$  \hspace{1cm} (2)

where $\gamma_{\text{hcp}}$, $\gamma_{\text{bce}}$, and $\gamma_{\text{hcp}}\sqrt{3}$ is the relaxed surface energy for the hcp $\langle 1\bar{1}20\rangle$ planes, the bce surface ($y$ plane in Zr NWs) energy and the bce-hcp interface energy, respectively. We note that at the beginning of transformation the volume change and total elastic energy are negligible in the immediate proximity of free surfaces. We therefore calculate $\gamma_{\text{hcp}}$ and $\gamma_{\text{bce}}$ by constructing a slab with $y$ plane as the exposed surface and periodic boundary condition along the other two directions and performing a global minimization using a conjugate gradient (CG) algorithm at 0 K, and we obtain the values of $\gamma_{\text{hcp}}$ and $\gamma_{\text{bce}}$ from the energy per area in excess of that of the slab without free surfaces. Similarly, the $\gamma_{\text{hcp}}\sqrt{3}$ is calculated by constructing an hcp-bce interface based on the Burgers OR (Ref. 5) and minimizing the system energy along the direction that is normal to the interface using the same CG algorithm. The calculated values of $\gamma_{\text{hcp}}$, $\gamma_{\text{bce}}$, and $\gamma_{\text{hcp}}\sqrt{3}$ at 0 K are 9.62, 9.17, and 0.10 eV/\text{nm}^2 respectively, which proves the validity of Eq. (2).

Unlike surface melting, in which the interface between liquid and solid is incoherent, the IMT-formed bce and the original hcp form a coherent phase boundary. The bce phase first occurs on the $\langle 1\bar{1}20\rangle$ surface planes, and propagates toward the ends and the interior of the NW, and then forms two opposite wedge-shaped areas with an interface boundary by rotating 30° along axis direction (schematically shown in Fig. 3). Therefore, the Helmholtz free energy difference $\Delta F$ between the hcp NW with bce structure in $\langle 1\bar{1}20\rangle$ planes, and an entirely hcp NW, can be given by

$$\Delta F = \frac{1}{2} \delta t \Delta F_{\text{hcp}}\text{volume} + 4\alpha t \gamma_{\text{hcp}} + \delta t (\gamma_{\text{bce}} - \gamma_{\text{hcp}})$$

$$+ \delta t (\gamma_{\text{hcp}} - \gamma_{\text{hcp}}\sqrt{3}),$$  \hspace{1cm} (3)

where $\delta = 2\sqrt{3}t$, $t$ is the thickness and $a$ the side length of
the wedge-shaped nucleus (see Fig. 3), respectively. In addition, \( \Delta F_{\text{volume}}^{\text{bcc-hcp}} \) (2.22 eV/nm\(^2\) or 0.052 eV/atom at 0 K) refers to the energy difference between bulk bcc and hcp crystals, which is actually the potential energy difference between bcc and hcp crystals at 0 K. \( \gamma_{\text{hcp}} \) and \( \gamma_{\text{bcc}} \) refer to the relaxed surface energies of \{0001\} hcp and \{011\} bcc in \( z \) planes, which are 8.00 eV/nm\(^2\) and 8.14 eV/nm\(^2\) at 0 K, respectively. As shown in Fig. 3, the two-step MT path has RT, its energy barrier is presumably very low. As for the three stages: the IMT, bcc distortion and bcc-to-hcp MT. As shown in Fig. 4, we see that \( \Delta F \) is closely related to the dimensions \( t \) and \( a \) of the bcc nuclei. For a fixed \( a \) value, \( \Delta F \) should be a function of \( t \). Before the occurrence of bcc, \( t=0 \). With increase in \( t \), \( \Delta F \) decreases which indicates that the IMT occur spontaneously. However, the obstacle terms [the first three terms of Eq. (3)] increase quickly with the growth of bcc nuclei and will gradually overpower the driving terms [the last term of Eq. (3)]. That is, there is a critical thickness \( t^* \) at which \( d(\Delta F)/dt=0 \). By the time \( t \) reaches \( t^* \), the bcc phase has no more incentive to grow, since \( \Delta F \) will start to rise. The IMT is thus self-limiting, stopping once the size of the bcc phase reaches a critical length scale. For \( a=2.1 \) nm, \( t^*=0.07a \) at 0 K but increases with increasing temperature as \( \Delta F_{\text{volume}}^{\text{bcc-hcp}} \) becomes smaller.

We have also verified that IMT in Zr nanowire is caused by the absolute surface energy difference, not the compressive stresses inside the nanowire due to surface stress. That is to say, were there no surfaces, but only infinite bulk hcp and bcc crystals, there can be no hcp \( \rightarrow \) bcc transformation even if a constant external stress (of equal magnitude as that due to surface stress in the nanowire) is applied.

Fcc or bcc NWs are known to undergo lattice reorientation via twinning (motion of twin boundaries)\(^8\) to minimize their surface energy. It is therefore important to address the question why the Zr NW prefers the two-step IMT-MT route, i.e., IMT from \{1100\} hcp to bcc and normal MT from bcc to \{1120\} hcp, rather than the direct twinning between \{1100\}-oriented and \{1120\}-oriented configurations. To this end, we calculate and compare the energy barrier at 0 K for each path. As shown in Fig. 2, the two-step MT path has three stages: the IMT, bcc distortion and bcc-to-hcp MT. As the forward normal MT is known to occur easily for Zr at RT, its energy barrier is presumably very low. As for the IMT, the hcp-bcc transformation is just the opposite of the normal bcc-hcp MT that combines shear and shuffle operations. The energy landscape is mapped out in Fig. 3(a) to find the energy barrier for IMT, as a function of shear and shuffle parameters. We find that the IMT easily occurs along the diagonal where the minimum energy barrier is 0.052 eV/atom. As far as the bcc distortion is concerned, the \{011\}-axis configuration undergoes distortion to \{100\}-axis configuration with shrinkage along \( x \)\{-101\}, expansion along \( y \)\{010\} and almost no change in \( z \)\{-101\}, and the volume remains almost constant during the process. We can then obtain the potential energy as a function of lattice parameter ratio from \( \sqrt{2}/2 \) (\{011\} configuration) to \( \sqrt{2} \) (\{100\} configuration), similar to the Bain transformation.\(^19\) As shown in Fig. 3(b), the energy barrier for such bcc distortion is 0.021 eV/atom. It is noted that, the energy landscape for IMT and bcc distortion are calculated at 0 K with periodic boundary conditions, and there is no relaxation during the movement of atoms.

We calculate next the energy barrier by direct twinning from \{1100\} hcp to \{1120\} hcp. The two configurations can form a \{2110\}/\{1100\}-type twin system with two types of twin boundaries (TB1 and TB2 as shown in Fig. 4(c)). Unlike fcc and bcc metals, both shear and shuffle are needed to for twinning in hcp. The shear (along \{2110\} and \{1210\} directions) changes the angle from the 60° in \{1100\} hcp to the 120° in \{1120\} hcp, and the atomic shuffle moves atoms...
by $a_0/3$ along the $[\bar{2}1\bar{1}0]$ direction [as illustrated in Fig. 4(d)]. Similar to the calculation for the IMT path, an energy contour map for this path at 0 K is plotted in Fig. 4(e), giving the minimum energy barrier as 0.213 eV/atom. The comparison schematically shown in Fig. 4(f) clearly indicates that the two-step MT is a much more energetically favorable path than direct twinning.

**IV. CONCLUSION**

In summary, in hcp Zr NWs the surface-energy reduction drives a hcp→bcc IMT, in contrast to the usual bcc→hcp MT that is driven by the volume bulk energy. Our MD simulations show that the initially ⟨110⟩-oriented hcp NW first undergoes IMTs into surface-bound bcc domains, and the metastable bcc domains subsequently meet, react and undergo normal MT to another ⟨1120⟩-oriented hcp configuration, resulting in the reorientation of the NW. Because the characteristic size scale of the system, i.e., diameter of the NW, is comparable to the self-limiting-length scale $r^*$ of IMT, the IMT can penetrate the wire, triggering the next stage of normal MT. In much thicker surface-bound slabs where $H \gg r^*$, we expect IMT to be self-limiting (at least in the thickness direction), which is fundamentally different from normal MTs in the bulk.

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